International Journal of Modern Science and Technology
http://www.ijmst.co/
Vol. 1, No. 6, Sept. 2016. Page 213-217.
ISSN: 2456-0235

Research Article

Effect of surfactant on the synthesis and characterization of ZnO nanoparticles and its photocatalytic activity

R. Bomila*, S. Srinivasan

Department of Physics, Presidency College, Chennai -600005. India.

*Corresponding author's e-mail: bomilar.m.sc@gmail.com

Abstract

ZnO nanoparticles were prepared via wet-chemical method in methanol / octylamine / zinc acetate as starting materials. To prepared sample was subjected to structural morphology elemental, optical properties were characterized by X-ray diffraction, UV-Vis spectroscopy, High resolution - Scanning electron microscopy. The photocatalytic activities were evaluated by the degradation of Methyl Orange dye under sun irradiation. The individual effect of photocatalytic activity of pure and surfactant influenced ZnO nanoparticles were done in degradation of organic pollution.

Keywords: ZnO nanoparticles; Octylamine; Structural, Optical properties; Photocatalytic activity.

Introduction

Recently semiconductors materials have attracted increasing attention due to wide range of application such as physiochemical properties [1]. Semiconductors photocatalysts offer great potential for complete elimination of toxic chemicals in environment through its efficiency and broad applicability [2-4]. For the removal of dye pollutants these semiconductors photocatalysts was applicable to a wide range of organic synthetic dyes. Semiconductors metal oxide such as CdS, Fe_2O_3, TiO_2, ZnO, ZnS nanoparticles (NPs) have most promising materials in the field [5-7]. Among these ZnO NPs has been recognized as photocatalysts in recent years. This was described to their inexpensive, nontoxic, environmental friendly, very effective semiconductor photocatalysts and biodegradation. When a semiconductor particle was irradiated by sun light with equal to or higher than the band gap energy on electron from the valence band (VB) was excited to the conduction band (CB) in aqueous media. The photocatalytic performance was excellent in the presence of electron acceptor such as H_2O_2.

However, the rate of electron- hole (e-h) recombination during photocatalytic process limits the application of these materials under sun irradiation [8-10]. It was well known that nanosized photocatalysts should be separated and recycled after photodegradation reaction. Furthermore, nanosized particles having large surface energy when recycled by using traditional separation method. In the past decade, a number of studies in TiO_2 and ZnO, both in the pure form or as a composite were semiconductor oxide widely used in photocatalytic activity [11]. Therefore improving photocatalytic activity by modification has become an important task among researches in recent years. The structure of nanomaterials, including morphology, particle size and two–dimensional and three–dimensional architectures, can play important roles in determining the electrical, optical and catalytic properties. The morphology, particle size, crystal orientation, crystallinity and oxygen defects are some factors that influence the photocatalytic performance and stability of ZnO photocatalysts.

The enhanced photocatalytic activity of the nanomaterials compared to pure ZnO, surfactant influenced ZnO were described to the large surface area, increased oxygen vacancy and the facilitation of diffusion and mass transportation of the reactant molecules [12]. Much work has focused an using organic surfactant or functional polymers as supports, but the presence of organic residues may reduce particle surface activity and thus limit its catalytic activity. There have been some reports on the synthesis of ZnO nanoparticles with organic supports such as dodecylamine, PVP, oleic acid and so on [13].

To promote the formation of ZnO nanostructures, Octylamine was using long-chain surfactant as a result in the decrease of the particle's surface energy. In the present investigation, the effect of surfactant was prepared by wet-chemical method and their

Received: 01.09.2016; Received after Revision: 09.09.2016; Accepted: 10.09.2016; Published: 12.09.2016

structural, morphology, optical and the photocatalytic activity by degradation of methyl orange (MO) solution under full solar spectrum absorbance in aqueous water.

Materials and methods

Materials

In this typical synthesis, Zinc acetate dehydrate (0.1 M) and Octylamine (1.32 mL) were added into absolute methanol (100 mL) stirring over 24 hrs. Following complete dissolution of the precursor a NaOH / distilled water solution (50 mL, 3 M) stirring for 4hrs. The prepared NaOH solution was added drop by drop in zinc acetate dehydrate, till the pH of the solution attains 12.The stirred solution was taken in a beaker and rinsed by ethanol / water to remove the precursor material. Finally we dried the suspension in Oven at 80 °C for 10 h and annealed for 400 °C for 2h.For comparison, pure ZnO nanoparticles were also synthesized in the same procedure without using surfactant. All the reagents used in the experiment were analytically pure and they were used as such without further purification.

Characterization

Powder X-ray diffraction (PXRD) recorded at room temperature on a (PAN analytical X'Pert PRO with 2θ ranging from 20° to 80°, X-ray diffractometer using Cu Kα irradiation (wavelength: 1.54056 Å)). In HR-SEM/EDAX , image of the sample was observed by using JEOL,JSM-67001.The optical absorption and photocatalytic degradation spectra was recorded by UV-Vis absorption spectrometer Perkin Elmer (T90 + Spectrophotometer).

Photocatalytic activity

The Photocatalytic activity of the as-synthesized pure and surfactant influenced ZnO nanoparticles by using Methyl orange (MO) textile dye, its photocatalytic activity was carried out in a solar light with de-ionized water. The catalytic experiments were carried out with 100 mL solution of MO (5 X 10^{-5} M) and 20 mg of the ZnO catalyst, dye solution was stirred in the dark for 30 min. After, the dye degradation test was carried out without stirring. For studying the kinetics of the degradation reactions,3 mL of the aliquot solution was withdrawn at regular time intervals, which was UV-Vis spectrophotometer by measuring the absorbance of the solution samples at λ = 434 nm. The degradation percentage of the dye performance can be calculated from the equation (1) [14].

$$\% D = (C_0 - C_t)/C_0 \times 100 \qquad (1)$$

Where,

C_0= Initial concentration of dye

C_t= Concentration of dye after irradiation in selected time interval

Results and discussions

X-ray diffraction analysis

The crystal structure of ZnO NPs was characterized with XRD pattern of the as-synthesized pure and surfactant influence ZnO NPs as shown in Fig. 1 (*a*, *b*) in the 2θ diffraction angle . From the Fig. 1 (b) shows the XRD patterns of ZnO NPs with surfactant nanostructures having eight sharp peaks at 31.82°, 34.44°, 36.26°, 47.52°, 56.45°, 62.68°, 66.08°, and 67.71° which was corresponding to different planes of pure ZnO. The results were in good agreement with the JCPDS Card: 36-1451 [15]. It shows that after adding surfactant there is no any extra peak in the XRD pattern confirming purity of surfactant ZnO NPs.

The high intensity of d_{101} plane as compared with other planes clearly suggests the preferential growth of ZnO nanoparticles along the c-axis direction. The strong and narrow diffraction peaks indicate that the material has a good crystallinity. It indicates surfactant has been incorporated into different sites of ZnO. The size of the particles was calculated by Debye Scherrer's formula [16-17]. The average crystallite size was calculated by the equation (2).

$$D=K\lambda/\beta \cos\theta \qquad (2)$$

K is a constant equal to 0.89; λ is the X-ray wavelength (0.1540nm), β the full wavelength at half maximum and θ angle diffraction. The average estimated grain size of the nanoparticles was found to be increased from 36 to 26 nm for pure and surfactant ZnO.

Morphological studies

In order to investigate the morphologies of pure and surfactant influenced ZnO NPs was shown in Fig.2 (a, b). In both cases the particles on agglomerates with effect of surfactant and solvent. The surfactant reagent relatively controls the uniform growth of nanoparticles with solvent and concentration. Surfactants

influenced ZnO NPs possess reduce size.HR-SEM images results were compared with XRD results was a good agreement of particles size for both the studies. Fig.2 (c, d) the elemental composition of the as-synthesized nanoparticles was characterized by EDAX . Almost all the peaks on the curves were described to Zn, C and O elements. Thus it was concluded that no other impurities at the detection levels.

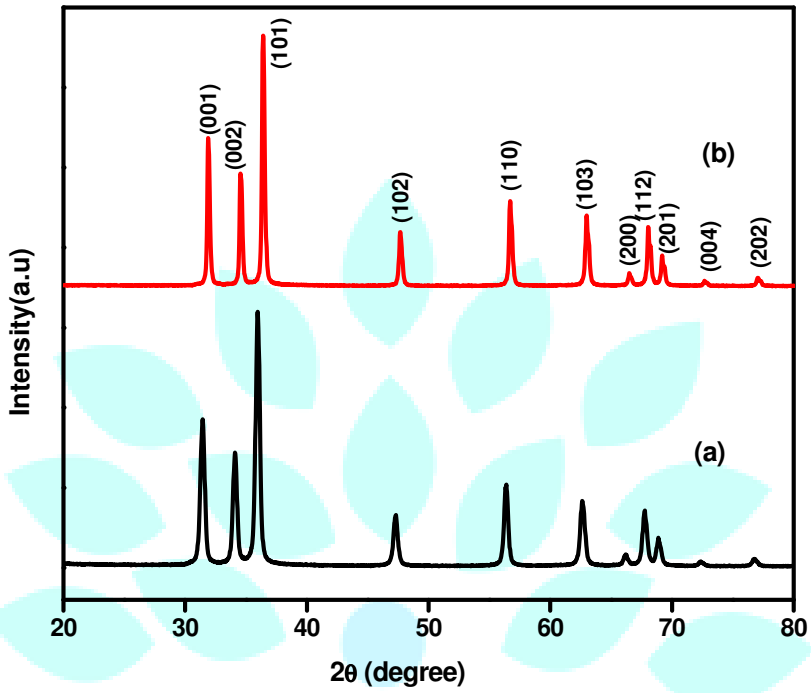

Fig. 1. XRD patterns of (a) pure (b) surfactant influenced ZnO NPs

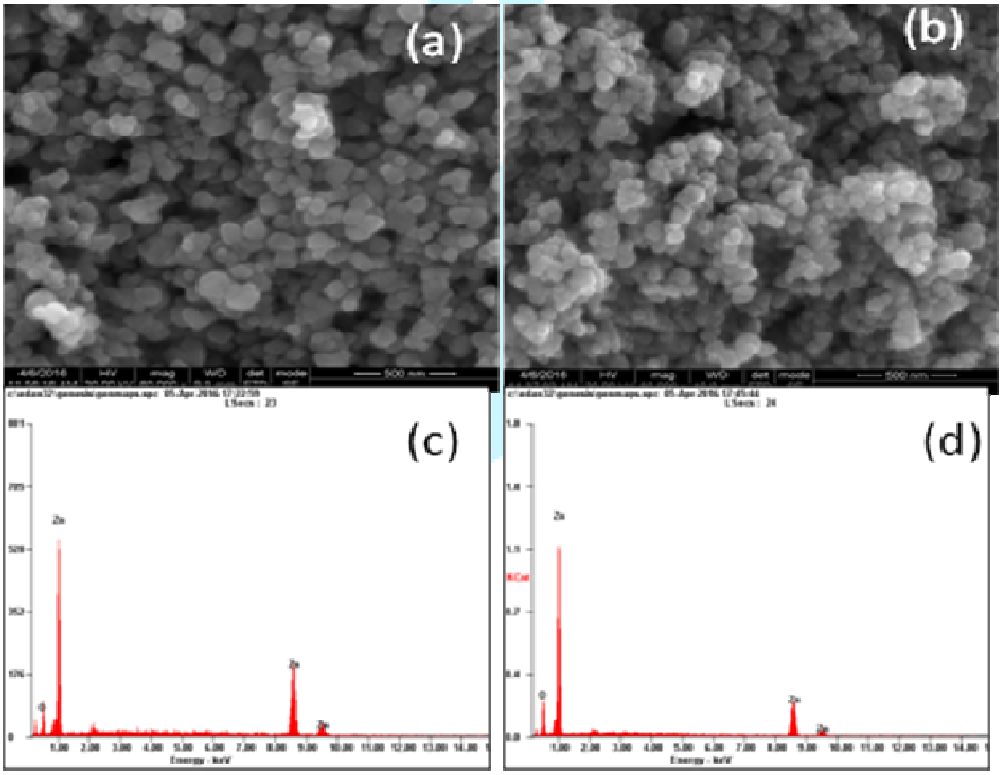

Fig. 2. HR-SEM/EDAX images of (a,c) pure and (b,d) surfactant influenced ZnO NPs

UV-Vis Spectrum

UV-Visible spectrum of as-synthesized pure and surfactant influenced ZnO NPs in the range of 300 nm - 600 nm presented in Fig. 3 (a,b) .We observe a small blue shift of the peak compared to pure ZnO due to quantum confinement of charge carriers. When the size of surfactant influenced ZnO NPs decreased, the band gap energy increased which in turn led to higher redox potential in the system. Therefore, the nanoscale ZnO was expected to have higher photocatalytic activity than its bulk [18].The calculated band gap values lie in the range of (3.22 eV and 3.25 eV) has been calculated by using Tauc's relation [19]. The band gap as a function of surfactant influence ZnO was shown in Fig.3 (c, d).The increases in band gap with surfactant influence ZnO NPs was attributed to size quantization effect due to the smaller size of the particles.

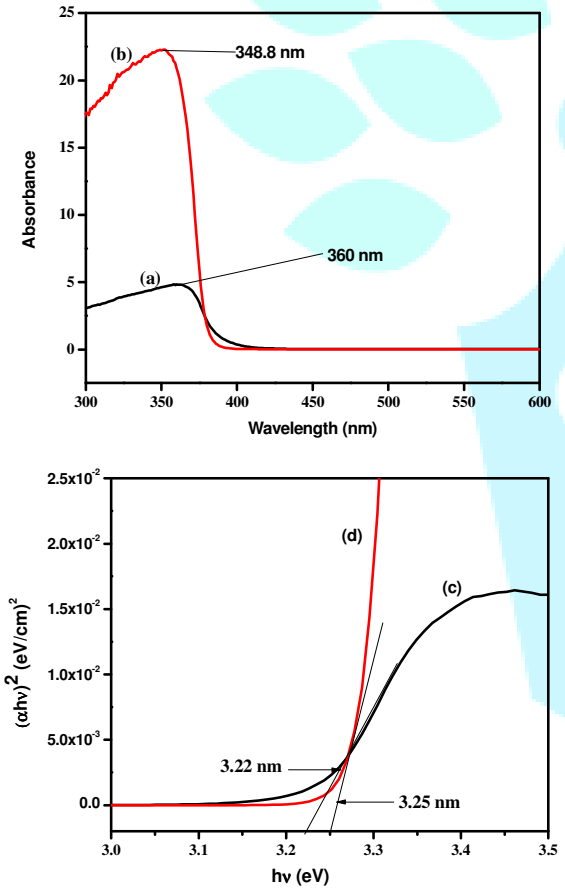

Fig. 3. UV-Vis absorption spectra of (a) pure (b) surfactant influenced ZnO NPs and (c, d) Tauc's plot for pure and surfactant influenced ZnO NPs

Photocatalytic activity

In this work, the activities of pure and surfactant influenced ZnO were evaluated for the photocatalytic degradation of Methyl orange (MO) under sun light was examined. As can be seen, degradation of MO using pure and surfactant influenced ZnO nanoparticles prepared in pure de-ionized water as solvent can occurs at 180 min.

The kinetic plot of log (C/C_0) vs. time (T) as shown in Fig. 4.Thus ,the results clearly reveal the individual effect of crystallite size and particle size favor higher photocatalytic activity when the rate constant of surfactant influence ZnO nanoparticles were compared to pure ZnO [20].

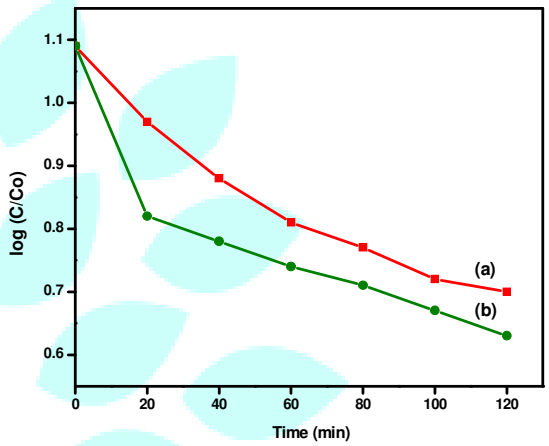

Fig. 4. Photocataytic studies of (a) pure (b) surfactant influenced ZnO NPs

Conclusion

The photocatalytic de colorization of a Methyl orange (MO) textile dye has been investigated using as-synthesized pure and surfactant influenced ZnO NPs under sun irradiation. This process reduces the recombination of light generated electron–hole pairs at ZnO surface. The results indicated that pure ZnO was more efficient than surfactant ZnO. The excellent performance of surfactant ZnO NPs in photo degrading organic dye was significant for the air and water pollution. XRD and HR-SEM demonstrated that the crystallite size ~ 16 nm to 14 nm and morphology of ZnO NPs was agglomerated spherical in shape were investigated. UV-VIS spectra were calculated band gap energy 3.22 eV – 3.25 eV slightly increases compared with pure ZnO NPs, it indicated blue – shifted in the quantum confinement.

Conflict of interest

Authors declare there are no conflicts of interest.

References

[1] Becker J, Raghupathi KR, Pierre JS, Dan Zhao D, Ranjit TK. Tuning of the crystallite and particle sizes of ZnO nanocrystalline materials in solvothermal synthesis and their photocatalytic activity for dye degradation. J Phys Chem C 115 (2011) 13844-13850.

[2] Xu F, Zhang P, Navrotsky A, Yuan ZY, Ren TZ, Halasa M, Su BL. Hierarchically Assembled porous ZnO nanoparticles: synthesis, surface energy, and photoacatalytic activity. Chem Mater 19 (2007) 5680-5686.

[3] Salem IA, El-Maazawi MS. Kinetics and mechanism of color removal of methylene blue with hydrogen peroxide catalyzed by some supported alumina surfaces. Chemosphere 41 (2000) 1173-1180.

[4] Poulios I, Micropoulou E, Panou R, Kostopoulou E. Photo oxidation of eosinY in the presence of semiconducting oxide. Applied Catalysis B 41 (2003) 345-355.

[5] Lizama C, Freer J, Baeza J, Mansilla HD. Optimized photodegradation of Reactive Blue 19 On TiO2 and ZnO suspensions. Catalysis Today 76 (2002) 235-246.

[6] Yu J, Zhang L, Cheng B, Su Y. Hydrothermal preparation and photocatalytic activity of hierarchically sponge-like macro-/mesoporous titania. J Phys Chem C 111 (2007) 10582-1058.

[7] Jing L, Wang D, Wang B, Li S, Xin B, Fu H, Sun J. Effects of noble metal modification on surface oxygen composition, charge separation and photocatalytic activity of ZnO nanoparticles. J Mol Catal A 244 (2006) 193-200.

[8] Yu J, Liu S, Yu H. Microstructures and photoactivity of mesoporous anatase hollow microspheres fabricated by fluoride-mediated self-transformation. J Catal 249(2007)59-66.

[9] Liqiang J, Dejun W, Baiqi W, Shudan L, Baifu X, Hongganga F, Jiazhong S. Effects of noble metal modification on surface oxygen composition, charge separation and photocatalytic activity of ZnO nanoparticles. J Mol Catal A 244 (2006) 193-200.

[10] Behnajady MA, Modirshahla N, Shokri M, Zeininezhad A, Zamani HA. Enhancement photocatalytic activity of ZnO nanoparticles by silver doping with optimization of photodeposition method parameters, J Env Sci Hea 44(2009)666-672.

[11] Pant B, Pant HR, Barakat NAM, Park M, Jeon K, Choi Y, Kim HY. Carbon nanofibers decorated with binary semiconductor (TiO_2/ZnO) nanocomposites for the effective removal of organic pollutants and the enhancement of antibacterial activities. Cer Inter 39 (2013) 7029-7035.

[12] Ye C, Bando Y, Shen G, Golberg D. Thickness-dependent photocatalytic performance of ZnO nanoplatelets. J Phys Chem B 110 (2006) 15146-15151.

[13] Li Y, Li X, Yang C, Li Y. Ligand-controlling synthesis and ordered assembly of ZnS nanorods and nanodots. J Phys Chem B 108 (2004) 16002-16011.

[14] John Becker,Krishna Reddy Raghupathi,Jordan St.Pierre,Dan Zhao, T.Ranjit,Koodali. Tuning of the crystallite and particle sizes of ZnO nanocrystalline materials in solvothermal synthesis and their photocatalytic activity for dye degradation. J Phys Chem C 115 (2011) 13844-13850.

[15] Jayakumar OD, Salunke HG, Kadam RM, Mohapatra M, Yaswant G, Kulshreshtha SK. Magnetism in Mn-doped ZnO nanoparticles prepared by a co-precipitation method. Nanotechnology 17 (2006) 1278-1285.

[16] Kumar SS, Venkateswarlu P, Rao VR, Rao GN. Synthesis, characterization and optical properties of zinc oxide nanoparticles. International Nano Letters 3 (2013) 30.

[17] Priya M, Elumalai M, Kiruthika S, Muthukumaran B. Influences of supporting materials for Pt-Ru binary catalyst in ethanol fuel cell. Int J Mod Sci Technol 1(2016)5-11.

[18] Sridevi D, Raj. KV. Synthesis and optical characteristics of ZnO nanoparticles. Bull Mater Sci 32 (2009) 165-168.

[19] Saaedi A, Yousefi R, Sheini FJ, Cheraghizade M, Zak K, Huang NM. Optical properties of group-I- doped ZnO nanowries. Cer Inter l 40 (2014) 4327-4332.

[20] Wahab R Hwang IH, Kim YS, Musarrat J, Siddiqui MA, Seo HK, Tripathy SK, Shin HS. Non-hydrolytic synthesis and photo-catalytic studies of ZnO nanoparticles. Chem Eng J 175 (2011) 450-457.

*****

